Applicability of Megacycle Frequency Oscillator Circuits

to Reaction Rate Measurement

by

Philip J. Elving

Technical Report No. 3

to the

OFFICE OF NAVAL RESEARCH

Under Project No. NR 051-318

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ABSTRACT

The basis for the application of megacycle frequency oscil-
lators to the measurement of rapid reaction rates is described, in
particular where insulated cells are used, i.e., cells in which
electrodes or other electrical connective devices are not in con-
tact with the sample solution. The applicability to ionizable
systems in aqueous solution is stressed. In such media, the use
of a high-frequency oscillator permits rapid measurement of elec-
trical conductance since point to point balancing of a bridge is
unnecessary. In nonaqueous systems, megacycle oscillators can be
used to follow both conductance and dielectric constant change.

The general relation of high-frequency conductance and capaci-
tance to the usual low-frequency conductance is indicated. The
critical factors involved include oscillator type and frequency,
cell design, and sample composition. The general limitation on
the use of the technique is due to the fact that only one physical
property of the system is being measured.

The specific application of an oscillator circuit to follow-
ing the rapid alkaline hydrolysis of esters is described in some
detail to illustrate the methodology involved in studying ionic
reactions.

Coincident with the general development of instrumentation in analytical chemistry has been the adaptation of megacycle frequency oscillator circuits for use in concentration-measuring devices. Although a fair amount of work was done previous to 1940, especially on the measurement of dielectric constant as an analytical index, current interest dates back to Blake's[1] use of Q meters in 1945 and the study of tuned-plate tuned-grid circuits by Jensen and Parrack[2] published in 1946. The successful use by the latter of the high-frequency method in titration attracted considerable attention to the field.

The present discussion is primarily devoted to studies in insulated cells, i.e., cells in which there is no direct contact between the sample solution and the electrodes or other connective device. Mention is made of a few pertinent studies involving the use at high frequencies of conventional conductance and dielectric constant cells where the electrodes are in contact with the solution under measurement. Both classes of cells depend upon the same basic properties of the solution and are amenable to the same general type of interpretation.

Papers published since 1946 have been largely focused on the utilization of high-frequency oscillators as devices for the detection of the equivalence point in the usual types of titrimetric reactions; relatively little attention has been paid to their use as a means of measuring reaction rates, particularly in rapid reactions. A few workers have investigated and discussed the nature of the measurements made in high-frequency oscillator circuits. The one brief book[3] on the subject is almost entirely devoted to the author's own work.

PRINCIPLE OF OPERATION. The basic utilization of a megacycle oscillator as an analytical device consists of inserting the sample in a component of the oscillator circuit where it can be considered as affecting the capacitance, resistance and, perhaps, inductance of the circuit. Specifically, the sample can be inserted in a cuvette placed between condenser plates, in a beaker resting on a plate and circled by a band, in a tube encircled by two band plates, in a tube surrounded by a coil, etc., where the condenser or coil is part of the oscillator circuit or is connected to the "unknown" terminals of an impedance-measuring circuit. The operation then essentially consists of (a) initially tuning the circuit to resonance, i.e., sustained oscillation, or some other reference state, with the sample cell either empty or containing a reference system; (b) introducing a sample into the cell; and (c) determining the resulting change in the circuit. The latter can be done in a variety of ways, e.g., by (a) returning the circuit to resonance through a variable capacitor in parallel with the sample and noting the capacitance change, (b) measuring the change in the plate or grid current or voltage of the oscillator tube, or (c) determining the change in frequency; the latter can, if desired, be converted into a voltage. Consequently, from the viewpoint of reaction rate measurement, it is possible to record current or potential as a function of time, using available automatic techniques. Based on suitable calibration, the resulting variation can be converted to concentration for kinetic calculations; if the current or potential variation is linearly related to concentration, the measurements can obviously be directly used for kinetic calculations.

PHYSICAL BASIS OF THE TECHNIQUE

A number of analyses of the nature of the electrical property being measured in the case of chemical systems by megacycle oscillator circuits have been attempted. The typical response given by aqueous solutions with changing concentration of electrolyte is shown in fig. 1; frequency-measuring circuits give an S-shaped response, while current-measuring instruments give a hump-shaped response; the positions of the maxima of the humps and the inflection points of the sigmoid curves vary with frequency for a given instrument, cell and solution.

The currently most acceptable treatment involves an explanation in terms of the equivalent circuit and the low-frequency conductance. The following discussion is based on that of Blaedel,[4-6] Blake,[1,3,7] Hall,[8-10] and Reilley and McCurdy,[11] who have contributed the most meaningful interpretations.

The sample system can be considered in terms of the equivalent circuit of fig. 2 where C_1 is the capacitance determined by the metal electrodes outside the glass dielectric of the sample cell, the cell wall and the inside surface of the glass wall. C and R represent, respectively, the capacitance and the resistance offered by the solution in the cell. Such an equivalent circuit provides a satisfactory logical basis for discussion and can be simplified into a series or parallel equivalent circuit of C and R. Only the parallel circuit will be discussed as being the more commonly encountered effective case; both the parallel and series circuits are treated in detail by Reilley and McCurdy[11].

The capacitances, C_1 and C, can be considered as relatively constant for a given aqueous system and set of operating conditions. C_1 is constant, since it includes invariant situations. The value of C is dependent upon the dielectric constant of the solution; its constancy is then indicated by the experimental fact that the dielectric constant of an aqueous solution is virtually unchanged in the normal concentration range, since it shows only a second order dependence on electrolyte concentration in dilute solution. Actually, the variation in C_1 and C may be considerable during a change in electrolyte concentration due to lack of cell symmetry and shielding[12].

The high frequency capacitance and conductance of a cell containing an aqueous solution have been shown[11] in the case of the parallel equivalent circuit of fig. 2 to be related by the following equation to the usual low-frequency, e.g., 1000-cycle, conductance of the solution and the dielectric constant of the solvent:

$$Y = \frac{(1/R)\omega^2 C_1^2}{1/R^2 + \omega^2(C + C_1)^2} + j\frac{\omega C_1/R^2 + \omega^3 C_1 C^2 + \omega^3 C C_1^2}{1/R^2 + \omega^2(C + C_1)^2} \quad (1)$$

where

Y is the net admittance (reciprocal of the impedance) of the circuit

R is the actual solution resistance, equal to $1/k$ where $K \to k$ is the actual low frequency conductance of the solution

ω is $2\pi f$ where f is the frequency

C_1 is the cell capacitance previously defined

C is the solution capacitance

j is the operator, $(-1)^{1/2}$.

Equation (1) is obviously in the form of the conductance-susceptance relation for a parallel a.c. circuit,

$$Y = G_p + jB_p \qquad (2)$$

where

G_p is the conductance term, $1/R_p$, i.e., the real part of admittance, where R_p is the equivalent parallel resistance

jB_p is the susceptance term (equal to $j\omega C_p$), i.e., the imaginary part of admittance

C_p is the equivalent parallel capacitance.

The experimentally observed results for concentration change (fig. 1) can be related to equation (1) as indicated in fig. 3, the data for which can be obtained by the use of a Twin-T impedance measuring circuit[10,11]. The latter effectively measures the equivalent parallel capacity and high-frequency conductance separately as well as independently of other circuit components. The values of the conductance at which the peaks and inflection points of fig. 3 occur can be related to the frequency, the values of C_1 and C, and the dielectric constant of the solvent. It is evident that fig. 1 and 3 are identical in form except for the log plot of fig. 1 and the inversion of the capacitance response.

The instruments which have thus far been described fall into three classes on the basis of the electrical property measured[9,11]: (a) measurement of high-frequency conductance or loss, (b) measurement of equivalent capacitance change, and (c) composite measurement of both equivalent capacitance and high-frequency conductance.

The coupling of dilute solutions to the circuit has been shown to be essentially capacitive. Consequently, greater sensitivity may usually be obtained if the glass sample cell is coupled by a band or plate arrangement.

It might be emphasized that for aqueous solutions the capacitance of the high-frequency cell differs from the capacitance across the solution in a conventional conductance cell in that the former is a function of the resistance of the solution, as can be seen from equation (1).

In general, as indicated, the nature and value of the property or properties measured are functions of sample composition, cell design, and oscillator type and frequency. It may be possible by a consideration of these factors as discussed in the references cited (especially 9 and 11) to select the optimum experimental arrangement for following the changes in any given system. For example, the concentration range for which a given experimental arrangement can be used can be readily ascertained by obtaining dilution curves of the type shown in fig. 1, as subsequently indicated.

Since most megacycle instruments described have used a very low power, the possible heating effect on the solution has not been a serious consideration; no other specific sources of error are apparently involved in the use of a radio-frequency field. Axtmann[13] found no effect on the reaction between ethyl alcohol and acetic anhydride in carbon tetrachloride solution when observed by a 2-megacycle frequency dielectric constant apparatus with metal plates in direct contact with the solution.

TYPICAL EMBODIMENT OF THE TECHNIQUE

The author and his coworkers in their earlier investigations used a tuned-plate tuned-grid circuit derived from that described by Jensen and Parrack.[2] Such a circuit has the advantage from the standpoint of reaction rate measurement of producing as the measuring item a current, I, which can be readily recorded by a recording potentiometer which utilizes the IR drop produced by the current in a known resistance, R.

The circuit and apparatus involved have been described[14]; the most important elements have been separated in the block diagram of fig. 4 in order that their functions may be more readily seen. A regulated power supply, A, provides the necessary voltage to the 10-megacycle oscillator, B. The jacketed reaction cell, C, is inserted in a coil forming part of a tank circuit in the oscillator. The response of the oscillator is measured through the potential drop in the resistance, R_2, which is communicated through the balancing circuit, E, and the shunt, F, to the recorder, G.

The use of a recorder to maintain a continuous and permanent record of the current change produced in the oscillator has considerably extended the use of the high-frequency technique in reaction rate measurement. A Brown Electronik recording potentiometer is satisfactory for observing reactions of half-lives of several seconds or greater. The instrument used has a 10-mv. range and requires 1.5 seconds for full-scale deflection.

Calibration curves relating (a) concentration and oscillator response (current in the example being discussed) and (b) the latter and recorder reading at different instrument sensitivities are readily obtained. For reaction rate calculation where recorder response corresponds linearily to concentration, calculations are conveniently made in terms of recorder units as subsequently indicated.

The response drift of the oscillator over a long period of time may be appreciable, owing to heating of the circuit elements, changes in humidity, line voltage fluctuations, etc. When the kinetic studies involve measurement over a relatively short period of time, such drift can be neglected. If it were desired to study slow reactions, the drift could easily be compensated for by previous determination or by periodic readjustment.

Small fluctuations in oscillator response during a reaction present no great difficulty if a recorder is used, as the fluctuations are easily discernible and the curve can be smoothed out. A steady and constant drift, on the other hand, may invalidate the results if the drift is not discovered. For this reason the current should always be observed closely for constancy prior to and after the running of the reaction.

The need for good grounding and shielding cannot be emphasized too greatly. Body capacitance may also be important; an investigator should always determine beforehand where he may safely handle the instrument without causing errors in the measurement.

KINETIC CALCULATIONS. In view of the perhaps novel nature of the experimental measurement, it may be worthwhile to indicate briefly how the data obtained for, e.g., a second-order reaction may be handled. For simplicity's sake, a linear relation between concentration and circuit response is assumed. The total change in recorder units is then proportional to the total concentration change. The latter is also equal to the initial concentration of the reactant present in the lesser amount, providing the reaction goes to completion. If the reading on the chart at time zero is i_o and the reading at infinite time is i_∞ then the initial concentration of the reactant present in the lesser amount, say b, is proportional to $i_o - i_\infty$ and the decrease after time t is proportional to $(i_o - i_t)/(i_o - i_\infty)$, i.e.;

$$x = \frac{i_o - i_t}{i_o - i_\infty} \, b = \sigma b \tag{3}$$

where $(i_e - i_t)/(i_e - i_\infty)$ is written as σ for convenience. Substitution of this expression in the usual equation for the rate constant for a second-order reaction and subsequent rearrangement give

$$t = \frac{2.303}{k(a - b)} \log_{10} \frac{1 - (\sigma b/a)}{1 - \sigma} \qquad (4)$$

A plot of t against the log term of equation (4) should yield a straight line, the slope of which is $2.303/k(a - b)$, for a second-order reaction.

Similarly, equation (3), if the initial concentrations are equal, results in the expressions

$$k = \frac{1}{at} \left(\frac{i_e - i_t}{i_t - i_\infty} \right) \qquad (5)$$

or

$$i_t = \frac{1}{ka} \left(\frac{i_e - i_t}{t} \right) + i_\infty \qquad (6)$$

so that a plot of i_t against $(i_e - i_t)/t$ should yield a straight line whose slope is $1/ka$. Equation (6) is particularly useful if the extrapolation of the curve of time $\underline{vs}$. response to infinite time is difficult, as a knowledge of i_∞ is not required. This may be the case for a very slow reaction.

If the reaction is very fast, it may be difficult to extrapolate the time-response curve to zero time. In this case, equation (5) can be rearranged to give

$$i_t = kat(i_\infty - i_t) + i_e \qquad (7)$$

where a plot of i_t against $t(i_e - i_t)$ should yield a straight line

of slope ka. The behavior of the reaction products, e.g., hydrolysis
of the salt produced in a saponification, may cause the plotted
relation to deviate from a straight line. In practice, the most
reliable results are obtained if the reactant concentrations are
chosen so that extrapolation to both zero time and infinite time
can be made. Equation (4) is then used for the kinetic calculations.

Some consideration has been given to the use of equations which
do not involve knowledge of i_e and, perhaps, i_∞. A method is being
developed[15] for the calculation of rate constants from the type of
data obtained with high frequency oscillators in the case of second-
order reactions. The principles of such an attack on the problem
were originally stated by Guggenheim[16] for first-order reactions.
A method for pseudo first-order reactions based on evaluation of
the slopes of the rate curve has been described[17].

APPLICABILITY OF THE TECHNIQUE

As far as the chemical application of megacycle frequency
oscillators is concerned, the emphasis has been mainly on the
study of inorganic reactions which exhibit inflection points such
as neutralization and precipitation titrations. Relatively little
attention has been directed toward the investigation of organic
systems other than for direct concentration measurement[18-22]
which involved essentially dielectric constant measurement[12], or
for titration[2,23], although the possibilities here should be obvious.
Any organic reaction which involves a change in the observed
electrical properties of the solution (due to conductance, dielectric
constant or some related combination effect) as a function of time,
may be conveniently studied. The essential criterion is that the

change in electrical property be an accurate indication of the
corresponding change in the composition of the solution. A
linear relation between electrical property change and concen-
tration would naturally be preferable for a simple interpretation
of the results and may be a requirement for second and higher
order reactions.

Some work has been done on following the composition of
flowing streams, which is obviously a problem closely related
to that of observing reaction rates. In several cases, the
measurement was essentially a conventional dielectric constant
determination. By placing a portion of the column between the
plates of a condenser or an equivalent arrangement, the progress
of chromatographic development was followed[24,25]. The same
general technique has been applied to ion-exchange involving
aqueous solution[26]. A 2-megacycle oscillator has been used to
analyze continuously plant streams of paraffinic-aromatic hydro-
carbon mixtures, based on the overall difference in dielectric
constant between these two groups of compounds[27].

High-frequency oscillators of the type with which this
paper is concerned have been applied in several instances to
following moderately slow reactions. Duke, Bever and Diehl[28]
observed the rate of precipitation of barium sulfate. Jensen,
Watson and Beckham[29] followed the hydrolysis of ethyl acetate;
calibration for the nonlinear loading of the oscillator was
necessary because of the high concentrations used. The com-
mercially available Sargent Oscillometer which employs a frequency
discriminator circuit (5 Mc/s), has been used to follow the con-
version of nitroalkanes to the aci form in aqueous dilute sodium

hydroxide solution[30]. Using manual rebalancing, the reaction was studied under conditions where the half-life was about one minute; by the addition of a recorder, there is no reason to believe that much more rapid reactions could not be followed.

The only work on rapid reactions is apparently that of the author and his coworkers[14,15]; their work on ester hydrolysis is subsequently described in some detail. However, Calcote[31], in measuring flame speeds, used a tuned-plate tuned-grid oscillator (65 or 100 Mc/s) to detect ionization when the flame passed through a tank coil of the oscillator.

More work has been done in following reactions which do not necessarily involve ionic changes and which can be performed in nonaqueous system, i.e., the measurement of dielectric constant as an index to composition. The Sargent Oscillometer mentioned, which measures the capacitance of the sample cell, might be suitable since its readings can be readily converted into units of dielectric constant; the response of this instrument can be fed into a recording potentiometer.

The most thorough studies to date on the use of dielectric constant measurement in following fast reactions are those of Burrell, Majury and Melville[32,33], who used a recording capacitance bridge (50-60 Mc/s) to follow the change in dielectric constant as an indication of heat of reaction in an isolated system. Correction was made for the change in dielectric constant due to compositional change; the magnitude of the latter dielectric constant change was too small to permit sufficiently accurate rate calculation. The apparatus can record the non-stationary phase of chemical reactions, especially polymerization

reactions, on a cathode-ray oscilloscope with a sensitivity of 1 part in 10^8 in capacity and a time-resolution of the order of 1 millisecond; a recording voltmeter is used for slower reactions. The apparatus is particularly applicable to studying photochemically induced chain reactions.

SAPONIFICATION OF ESTERS. The basis for the application of a high-frequency oscillator to measuring the rate of alkaline hydrolysis of esters[14] is evident from the dilution curves of fig. 5, which indicate that at a concentration of 4 millimolar or lower the oscillator circuit concerned could be used for following the reaction between an ester and NaOH. Fig. 5 emphasizes the general relationship of the megacycle oscillator technique to ordinary conductometric technique in which it is assumed in measurement of this type of reaction that the change in conductance is linear and is due to a replacement of the hydroxyl ion by the anion of the acid from which the ester was derived. Ethyl alcohol and acetate are seen to contribute negligibly within the low concentration range.

The apparatus arrangement (fig. 4) was tested by measuring the rates of alkaline hydrolysis of the lower aliphatic esters since these compounds have been fairly thoroughly studied. The rate constants obtained[14] are compared in table 1 with previously determined values.

TABLE 1. COMPARISON OF REACTION RATE CONSTANTS (liter mole^{-1} sec.$^{-1}$) FOR ALKALINE HYDROLYSIS OF ALIPHATIC ESTERS AT 25° C.

	Acetate			Propionate	
	Salmi, Leimu[34]	Hammett[35]	Flom, Elving[14]	Salmi, Leimu[34]	Flom, Elving[14]
Ethyl	0.109	0.108	0.110	0.089	0.083
Propyl	0.087	0.098	0.095	0.079	0.072
Butyl	0.087		0.091	0.069	

Denbigh[36,37], using a flow method, found a rate constant for ethyl acetate of 0.110 liter mole^{-1} sec.$^{-1}$. In view of the widely differing types of measurement used for following the reactions, the agreement is considered to be good.

The rates of alkaline hydrolysis of the esters of halogenated acids have not been extensively investigated because of the high speed with which these reactions occur. Furthermore, as a result of the slight solubilities of these esters in water, it is not possible to operate at the usual concentrations used in the study of aqueous solution kinetics.

Skrabal and Rückert[38] studied the saponification of mono- and dichloroacetic esters in aqueous media, using a rather indirect measurement technique. A rate constant value of 136 liters mole^{-1} sec.$^{-1}$ was obtained for the alkaline hydrolysis of methyl chloroacetate. A more accurate, but still indirect, method was used by Bell and Prue[39], who obtained a lower value for methyl chloroacetate hydrolysis (65 liters mole^{-1} sec.$^{-1}$). A unique thermal method for following such reactions with half-lives in the range of 3 seconds to 3 minutes has been proposed, but has not yet apparently been applied to the reactions here under discussion[40].

It seemed that the rate constant could be more directly determined by following the concentration change with a recording high-frequency oscillator, the feasibility of which approach had been indicated by the investigation of the lower aliphatic esters. Use of an oscillator circuit would permit more dilute solutions to be studied, thereby lengthening the time of half-life of the reaction, and the concentration change could be measured instantaneously and continuously without the need for removing

samples, manipulating dials, or performing any additional
operations. The importance of the latter feature in the investi-
gation of fast rates involving rapid changes of solution conduc-
tance is obvious.

The values of the rate constants (liter mole^{-1} sec.$^{-1}$) for
the methyl and ethyl esters of the three chloroacetic acids at
20° are shown in fig. 6, where the length of each experimental
datum indicates the probable error. The rate is increased approxi-
mately tenfold for each additional chlorine atom added; the order
of increase is comparable for the methyl and ethyl esters.

An original experimental recorder trace and a rate constant
plot for the hydrolysis of methyl chloroacetate at 30° are shown
in fig. 7 and 8. The half-life in the particular experiment shown
was 13 seconds. The average half-lives at 20° for methyl and ethyl
dichloroacetates in this study were 8 and 12 sec., and for ethyl
trichloroacetate from 2 to 6 sec.

In studying the halogenated esters, NaOH solution was placed
in the cell and was diluted with water such that the final volume
after the addition of ester would be 175 ml. The stirrer was
started and the oscillator was tuned to a point on the steep
portion of the loading curve. The ester solution was then added
in 5-, 10-, or 20-ml. portions from a calibrated glass syringe.
The recorder was started either before or at the same time as
the delivery of the ester; a satisfactory curve trace usually
began within one second.

The tuned-plate tuned-grid oscillator circuit and experimental
arrangement used by Flom and Elving[14] have been modified so as
to permit the use of smaller sample volumes[15]; equal volumes of

the reactant solutions are delivered from 5 to 50-ml. hypodermic
syringes, being mixed within a jet chamber adapted from the types
originated by Roughton[41,42] and developed by Chance[42,43]. An
oscillator is now in the process of construction, to which the
sample cell consisting of a glass tube or capillary will be con-
nected by (a) bands around the tube, (b) conducting strips painted
on the inside or outside of the tube and protected by a coat of
insulating resin, or (c) some analogous coupling device. It is
hoped that this will permit more rapid attainment of a homogeneous
reaction system and hence the following of reactions of half-life
considerably less than a few seconds. Such a type of cell has
been recently mentioned in connection with the following of rapid
inorganic ionic reactions by conventional conductance measurement[44].
Apparently, Saal[45] was the first to adopt the Hartridge and Rough-
ton mixing technique to determining via conventional conducto-
metric and potentiometric measurement the time required for the
completion of ionic reactions; he has also indicated previous work
on the latter problem.

RELATIVE VALUE OF THE TECHNIQUE

The use of a megacycle or radio-frequency oscillator employing
insulated cells for conductance measurement has the major advan-
tages over the usual low-frequency conductance measurement of
(a) dispensing with the contact of the solution with electrodes
and its attendant difficulties, and (b) permitting more rapid
recording of concentration changes since point by point balancing
is unnecessary. On the other hand, it suffers from an apparent
greater complexity of interpretation. The necessary high-frequency
instrumentation is usually less elaborate and costly than that

required for equivalently precise low-frequency measurement.

Compared to other measurement techniques such as titration or spectrophotometry, the high-frequency technique has the inherent limitation of lack of specificity characteristic of any method of measurement based on a single physical property such as conductance, refractive index or volume. Strictly speaking, such measurement can be related to the composition or change in composition of only an effectively two-component system, i.e., (a) a system involving the replacement of one substance by another, (b) a system in which the relative values of the physical property being measured are such as to make the system a pseudo two-component mixture, or (c) a system in which the change in species is so connected relative to the values of the property concerned that one value of the property permits analysis of the system.

The megacycle-frequency technique can be used to follow ionic changes in aqueous solutions and dielectric changes in nonaqueous solutions where spectrophotometric or other analytical methods are not readily applicable.

In the case of aqueous solutions, the applicability of the high-frequency technique is limited to quite dilute solutions, i.e., to concentrations equivalent to 10^{-1} to 10^{-3} normal in electrolyte. This limitation, plus the fact that the response of the instrument is usually due to ionic conductance, effectively precludes the possibility of studying reactions in adequately buffered media; this is true of conductance methods in general. The wide applicability in nonaqueous media where effectively dielectric constant change is being measured, is indicated by the work of Burrell, Majury and Melville[32,33] cited. The possibility of investigating ionic reactions in nonaqueous media is shown by the successful titration of organic bases with $HClO_4$ in glacial acetic

acid using an oscillator (1 Mc/s)[23].

Reactions whose rates are too rapid to be followed by a recording potentiometer or similar device, could be followed by photographing the potential-time record traced on a cathode-ray oscilloscope.

The ultimate limitations to the megacycle-frequency technique would seem to be (a) the speed with which mixing of the reactants can be achieved and (b) the time factor involved in the response of the oscillator and recording circuits. The latter is not a limiting factor if oscillographic recording is used since the time delay in such response should never exceed a few microseconds.

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Fig. 1. Response of high-frequency oscillator circuits
as a function of concentration.

Fig. 2. Equivalent circuit.

Fig. 3. Relation of high-frequency conductance and
capacitance to low-frequency conductance.

Fig. 4. Block diagram of high-frequency oscillator apparatus
arrangement for reaction rate measurement.

Fig. 5. Effect of concentration change on oscillator response
for various compounds.
Water used as reference substance.

Fig. 6. Dependence of rate constant (liter mole^{-1} sec^{-1}) at 20° C.
on number of chlorine atoms in acidic portion of esters
of acetic acid.

Fig 7. Original recorder trace for alkaline hydrolysis
of methyl chloroacetate at 30° C.

Fig 8. Alkaline hydrolysis of methyl chloroacetate.
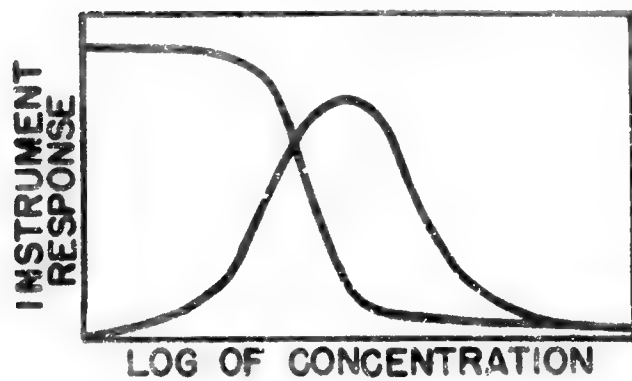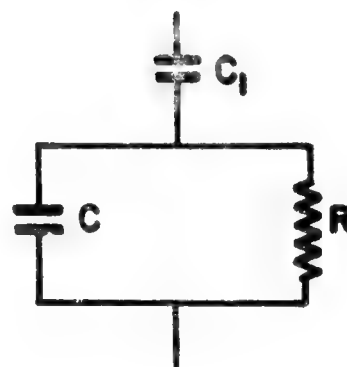Data derived from fig. 7.

FIG. 1

FIG. 2

FIG. 3

G
RECORDER

D
CONSTANT
TEMPERATURE
BATH

C

F

AYRTON
SHUNT

E
BALANCING
CIRCUIT

R_2

B
OSCILLATOR

A
POWER
SUPPLY

TIME, SEC.

CURRENT